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MAGNETORESISTANCE IN SINGLE CRYSTALS OF GRAPHITE

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ABSTRACT. Transverse and longitudinal magnetoresistance in single crystals of graphite have been studied at room temperature for currents both along and perpendicular to the basal plane. The effect of orientation of the magnetic field with respect to the direction of current as well as of the crystallo-graphic axis have also been studied. It has been observed that for both transverse and longitudinal cases with currents along or perpendicular to the basal plane, maximum magnetoresistance is obtained only when the magnetic field is parallel to the hexagonal axis. Magnetoresistance has been found to deviate from a H^2 (H being the magnetic field strength) law of magnetic field variation down to the minimum field available for this investigation, namely about 350 Oersteds.

INTRODUCTION

Magnetoresistance effects in crystals of graphite studied so far (Kinchin, 1953; Berlincourt and Steele, 1955; Soule 1958) have been only for currents along the basal plane and magnetic field mostly normal to the direction of the current (i.e. the transverse magneto-resistance effect only). But it has been shown by Krishnan and Ganguli (1939), Dutta (1953) Ubbelohde (1960), Primak and Fuchs (1954) and others that there is an appreciable amount of contribution to the electrical properties, from electrons or holes, (probably thermally excited) along the direction perpendicular to the basal plane. Further, it has been pointed out (Wilson 1954; Pearson and Suhl, 1951; Allgaier, 1958) that in cases of anisotropic semiconducting crystals longitudinal magnetoresistance i.e. change of resistance with magnetic field along the direction of the current, in specific directions of the crystal may be very large. even larger than the tranverse effect. It therefore appears necessary to study the transverse as well as longitudinal magnetoresistance effects in graphite crystals for currents along the *c*-axis as also the longitudinal effects for currents along the basal plane.

The present communication describes the results of measurements of magnetoresistance in these cases as also for different necessary and possible orientations of directions of electric current and magnetic field with respect to crystallographic axes. It is to be mentioned here that our observations are all for low magnetic fields and at room temperatures so that quantum effects are unobservable.

EXPERIMENTAL

When a material of electrical resistance R is placed in a magnetic field its magnetoresistance is given by $\Delta R/R$ where ΔR is the change of resistance caused by the magnetic field and can be observed in the following cases :

(i) When the magnetic field is parallel to the direction of electric current and its effect is measured in the direction of current.

(ii) When the magnetic field is perpendicular to the direction of current and the effect is measured in the direction of the current.

(iii) When the magnetic field is perpendicular to the direction of electric current and the effect is measured perpendicular to both current and magnetic field.

The case (i) above is the longitudinal magneto-resistance effect referred to in the previous section. Of the two remaining cases, the last one is nothing but the Hall effect. It will be noticed that a small misalignment of the Hall electrodes, in the measurement of the Hall effect, from exact normal direction to H and E will cause an appreciable superimposed effect from transverse magneto-resistance effect. From the remaining case i.e. case (ii) one can obtain transverse magneto-resistance effect directly. In our case we have usually measured the transverse magnetoresistance effect, adopting the arrangement of case (ii) though some measurements by the arrangement (*iii*) were also taken.

The specimens used were flakes of well developed single crystals of graphite obtained from Ceylon and carefully cut into suitable forms. In order to be sure that no appreciable crystalline defects are produced by these cutting treatments the specimens were examined by X-rays before and after such operations. The specimens are mounted in specially designed holders so that crystals of different sizes can be accommodated in them, maintaining at the same time the appropriate length to breadth ratio. Resistances were measured by the usual potentiometric method using a "Pye" precision vernier potentiometer reading down to one microvolt. Any thermal effects superposed on the effects studied were eliminated in the usual way.

The following sets of observations were taken in course of this investigation.

A. For currents in the basal plane of the crystal :

(1) direction of current vertical and magnetic field horizontal; rotation axis vertical (basal plane of crystal necessarily vertical)

(2) directions of current and magnetic field both horizontal; rotation axis vertical; basal plane vertical.

B. For current along the c-axis (perpendicular to the basal plane) :

(1) direction of current and magnetic field both horizontal; rotation axis vertical (basal plane necessarily vertical)

In all cases observations were taken for different angles between the c-axis and the magnetic field. It is to be noted that other dispositions of the crystal specimen in the magnetic field are possible, but a little consideration will show that these will lead to no new information.

RESULTS

Results of different observations are represented in Tables II to IV and in figures 1 to 4. In Table I, are represented for the sake of comparison, values of magnetoresistance obtained from direct observations also from Hall effect measurements. The values obtained by the two methods are more or less the same. So at room temperature we found no difference in the two methods of observation as was found by Berlincourt and Steele (1955) at low temperature.

TABLE I

Values of transverse $\Delta R/R$ obtained directly and from Hall effect measurements

Magnetic field strength in Oersteds	Transverse $\Delta R/R$ from direct observation; current in the basal plane	Transverse $\Delta R/R$ from Hall effect measurements; current in the basal plane
4000	.0630	.0685
3000	.0400	.0420
2000	.0190	.0195
1000	.0053	.0055
500	.0015	.0017

For currents along c-axis observed Hall e.m.f.s. being very small, magnetoresistance obtained after necessary corrections will not be accurate and hence has not been included in the Table I.

For currents along the basal plane maximum magnetoresistance is always observed when the angle between the magnetic field and the c-axis is zero, disposition of current and magnetic field being transverse to each other. But when current is perpendicular to the basal plane, though magnetoresistance is maximum when the above angle is zero yet the relative disposition of current and field instead of being transverse is parallel and the magnetoresistance we observed is a longitudinal one.

TABLE II

Variation of $\Delta R/R$ with the magnetic field and with orientation in the magnetic field. Current along basal plane and vertical; θ is the angle between c-axis and magnetic field

Magnetic field in Oersteds	$\Delta R/R$			
	$\theta = 0°$	$\theta = 30°$	$\theta = 70°$	$\theta = 90°$
7500	.1792	.1330	.0462	.0059
7175	.1657	.1242	—	—
6750	.1518	.1131	.0388	.0051
6350	.1356	—	·	—
5800	.1198	.0882	.0300	.0040
5100	.0938	—	—	—
4275	.0729	.0534	.0178	.0024
3400	.0473	.0344	.0116	.0014
2875	.0353	—	—	—
2300	.0243	.0173	.0059	.0008
1750	.0160	.0109	.0035	.0004
1175	.0069	.0057	.0018	.0002
600	.0019	.0014	.0003	—
350	.0007	.0005	.0002	—

TABLE III

Variation of $\Delta R/R$ with magnetic field and with orientation in magnetic field. Current along basal plane and horizontal, θ is the angle between c-axis and magnetic field

Magnetic field in Oersteds	$\Delta R/R$			
	$\theta = 0°$	$\theta = 30°$	$\theta = 60°$	$\theta = 90°$
7500	.1762	.1370	.0572	.0038
6750	.1485	.1163	.0470	.0033
5800	.1151	.0899	.0402	.0026
4275	.0692	.0543	.0219	.0017
2300	.0232	.0179	.0078	.0006
1175	.0068	.0054	.0023	.0001
350	.0005	.0005	.0002	—

TABLE IV

Variation of $\Delta R/R$ with magnetic field and with orientation in magnetic field. Current perpendicular to basal plane and horizontal. θ is the angle between current and magnetic field, i.e. between c-axis and the field.

Magnetic field in Oersteds	$\Delta R/R$			
	$\theta = 0°$	$\theta = 30°$	$\theta = 60°$	$\theta = 90°$
7500	.0421	.0327	.0135	.0008
6750	.0364	.0279	.0118	.0005
5800	.0281	.0214	.0090	The values became too low to be reliably measured with our potentio-meter.
4275	.0180	.0136	.0056	
3400	.0118	.0089	.0039	
2300	.0062	.0059	.0022	
1175	.0025	.0018	.0006	
350	—	—	—	

In order to test the observations of magnetoresistance for current along the basal plane and flowing in a vertical direction with the magnetic field horizontal, observations have also been recorded with a thin flake of graphite crystal having a minimum width as well as with a plate of extruded sample of graphite, the disposition of current and magnetic field being same as before. The importance of those observations will be discussed in the next section.

It may be pointed out here that for currents along the basal plane the magnetoresistance effects observed for the cases when the current is vertical and when it is horizontal are slightly different and is obviously a consequence of crystal anisotropy.

DISCUSSION

Before proceeding to discuss the various results of observations on the magnetoresistance effects in graphite, it should be borne in mind that graphite is a natural crystal and a considerable amount of mosaicity in structure is present in it in addition to foreign impurities. Any attempt to remove the foreign impurities increases the mosaicity further (Ray, 1959) which again considerably affects the different bulk properties of the crystal (Bhattacharya, 1959). Therefore all discussions on the observed properties of graphite will be under this limitation, that is, there is present an appreciable amount of mosaicity of structure in all crystals of graphite obtained from natural sources whether purified or not.

(i) *Current along the basal plane flowing in a vertical direction, magnetic field being horizontal and the rotation axis vertical*

Under this arrangement, for all orientations of the crystal with respect to the magnetic field, the latter is always transverse to the current. But the magnetoresistance observed changes (figures 1 and 4) as the angle between the

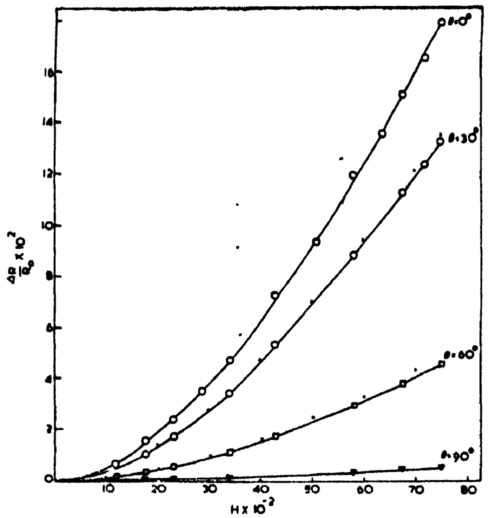

Fig. 1.—Variation of transverse $\Delta R/R$ with magnetic field H for different values of the angle between magnetic field and c-axis of the Crystal; current along the basal plane and vertical, field being horizontal. × × × Calculated points.

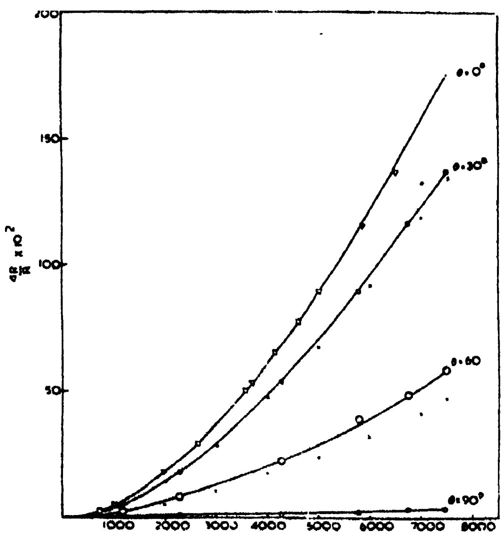

Fig. 2.—Variation of $\Delta R/R$ with H, the magnetic field for different values of θ; current along basal plane and horizontal; field horizontal. × × × Calculated points.

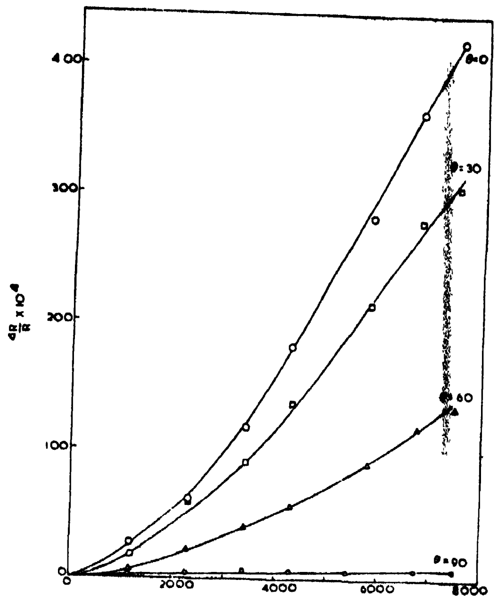

Fig. 3.– Variation of $\Delta R/R$ with H, the magnetic field for different values of current $\perp^r$ to the basal plane and horizontal, field also horizontal.

c-axis and the magnetic field changes, being maximum when this angle is zero and minimum when it is 90°. That this observation is a consequence of crystal anisotropy and not a size effect is verified by repeating the experiment with a crystal having a minimum width, when similar results were obtained; but when it was repeated with an extruded sample of graphite which is practically polycrystalline and whose dimensions are similar to those utilised for this investigation, magnetoresistance was found to remain practically constant for all orientations of the crystal with respect to the magnetic field. The observations may therefore be explained on the basis of high anisotropy of graphite due to which effective mass of the carriers for motion in the basal plane is, as is well known, (Shoenberg, 1952-53; Krishnan and Ganguli, 1941; Dutta, 1958) very small in comparison with that in directions parallel to the c-axis. Magnetoresistance which is inversely related to the effective masses of the electrons (or holes) will evidently be much larger in the basal plane than in a perpendicular direction. At any intermediate orientation the effect observed will be a resultant in that perticular direction of the components of the two extreme values, the effective part of the Lorentz force producing the effect being different for each orientation. In addition to these there will be a contribution from the magnetoresistance effects due to differently misoriented crystallites in the specimen. Our observed values are the statistical averages of all these.

In view of what has been stated above, magnetoresistance $\Delta R/R$ at any angle between the field and the c-axis will evidently be given by the relation of the type

$$\Delta R/R = A\cos^2\theta + B\sin^2\theta$$

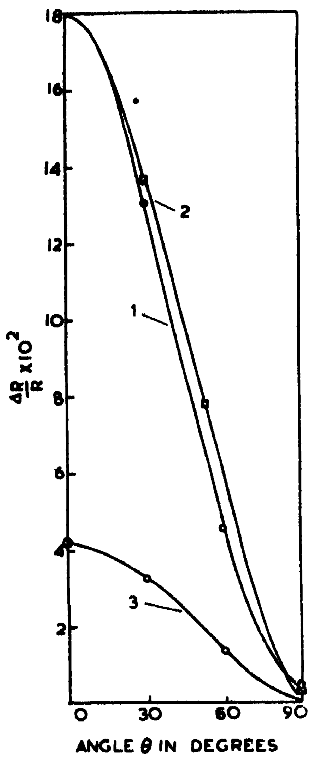

Fig. 4.—Variation of $\Delta R/R$ with θ for different directions of current. H = 7500 Oersteds.

Curve (1) Current parallel to basal plane and vertical, H horizontal, rotation axis vertical; arrangement always transverse.

Curve (2) Current parallel to the basal plane and horizontal, H horizontal, rotation axis vertical; arrangement transverse when $\theta = 0°$ and longitudinal when $\theta = 90°$.

Curve (3) Current perpendicular to the basal plane and horizontal, H horizontal, rotation axis vertical; arrangement transverse when $\theta = 90°$ and longitudinal when $\theta = 0°$.

where A and B are respectively the maximum and minimum values of magnetoresistance. The calculated values according to this relation are plotted in figures 1 and 2 alongside the curves showing the variation of observed $\Delta R/R$ with angle of orientation and with magnetic field. The slight deviations observed are due presumably to experimental missettings and misoriented crystallites present in the basal plane and whose contributions to magnetoresistance are not related in any simple way with the variations of θ and magnetic field, since in considering the contributions towards the principal magnetoresistance of the crystal both the transverse as well as longitudinal components from the different misoriented crystallites will have to be taken into account. This can however be done provided we know the number of misoriented blocks at any particular angle of misorientation. We have recently developed a method of doing this and the results obtained after employing the method are going to be published soon.

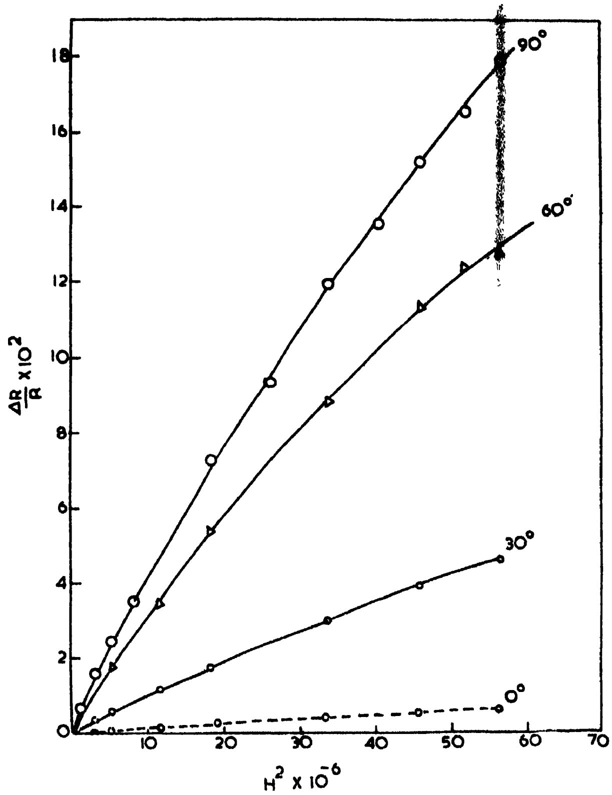

Fig. 5.—Variation of transverse $\Delta R/R$ with H^2 for currents along the basal plane and $\theta = 0°$

Before concluding this section it may be remarked that the very low value of $\Delta R/R$ observed when the angle between the c-axis and the field is 90° may be considered to be due not only to transverse magnetoresistance considerably diminished as a consequence of the bending of electron paths taking place in directions parallel to the c-axis of the crystal but also to contributions from missettings and misorientations of crystallites which are also very small.

(ii) *Current along the basal plane flowing in a horizontal direction, magnetic field being horizontal and rotation axis vertical*

The observations recorded (figures 2 and 4) in this arrangement are more or less of the same type as in (i) above with the exception that when the field and the current are parallel i.e. when the angle between the field and the basal plane is zero (angle between the c-axis and field is $90°$) the feeble magnetoresistance (much feebler than in the similar disposition with the transverse case discussed above) observed, is due to contributions from misalignment of crystallites in the basal plane, as well as longitudinal magnetoresistance in the basal plane.

(iii) *Current along c-axis flowing in a horizontal direction, magnetic field being horizontal and rotation axis vertical*

Magnetoresistance in graphite with this arrangement has not been studied earlier. The nature of variation of $\Delta R/R$ with the angle between field direction and current direction though more or less of the same type as discussed above yet differ in one important aspect. In all the earlier cases the transverse magnetoresistance was always much larger than the longitudinal one (see figure 4) but in this arrangement the reverse is the case (figure 3). Similar behaviour, namely longitudinal $\Delta R/R$ value greater than transverse one has been observed in semiconductors like n-type germanium (Pearson and Soule, 1951) and p- and n-type PbTe (Allgaier, 1958) for currents in some specified directions. Incidentally, it may be mentioned here that graphite behaves as a semiconductor for currents along directions parallel to the c-axis (Dutta 1953), currents being most probably mainly carried by holes (Ubbelohde *et al.* 1960).

In this connection it is interesting to note that whether the arrangement is transverse or longitudinal, magnetoresistance is maximum when the magnetic field is perpendicular to the basal plane for both directions of current.

(iv) *Variation of $\Delta R/R$ with Magnetic field.*

In order to test the usual H^2 law of variation of $\Delta R/R$ we plotted for current along the basal plane transverse $\Delta R/R$ against H^2 where H is the field strength in figure 5. It is observed that deviations are quite appreciable. These deviations may be either genuine or due to crystal defects present in the samples or both. However, from the logarithmic plot (figure 6) made for the purpose we obtained a $H^{1.69}$ variation for currents along the basal plane flowing in a vertical direction for higher fields 2000 to 7500 Oersteds and a $H^{1.88}$ variation for lower values of fields (350 to 2000 Oersteds). Similar is the case for currents along the basal plane flowing in a horizontal direction. When current is along directions parallel to the c-axis we could utilise the values of the longitudinal case, only, the transverse values being too small to be relied upon for any discussion. In the range of fields within which the observed values can be taken to be reliable the variation follows a $H^{1.62}$ law. Other workers (Kinchin, 1953; Berlincourt and Steele, 1955; Soule 1958), who also studied the field variation of $\Delta R/R$ obtained deviations from H^2 law. Their values can be summarised in the following table (Table V), our values also being included for comparison. Soule (loc cit.), who has made somewhat exhaustive study of the field variation of $\Delta R/R$ at room temperatures and low fields, suggests that deviation from H^2 law which takes

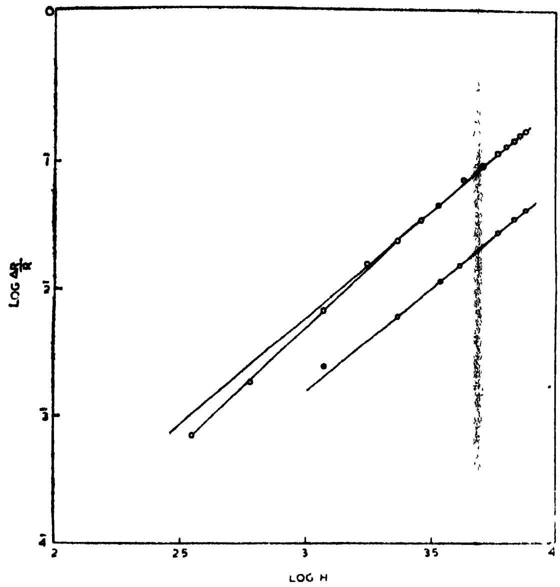

Fig. 6. Variation of log $\Delta R/R$ with log H.
Curve (1) Current along basal plane, $\theta = 0°$ (transverse)
Curve (2) Current $\perp^r$ to basal plane, $\theta = 0$ (longitudinal)

TABLE V

Values of p in the relation $\Delta R/R = BH^p$ obtained by different authors

Sample studied	Relative orientations of current and magnetic field	H^p Author: Berlincourt Steele (loc.cit)	Soule (loc.cit)	Kinchin (loc.cit)	McClelland (1955)	Present Author
Poly crystalline graphite	transverse	-	—	$H^{1.74}$ temp. 77°K to 290°K field not mentioned.	$H^{1.77}$ temp. 300°K Field-5-15 K.O.	-
Single crystal	transverse Current along basal plane, $H \perp^r$ to current	$H^{.80}$ at liq. He temp. field 25 K.O.	$H^{1.78 \pm 03}$ above 77°K $H^{.82}$ at liq. He temp. Field in both cases 25 K.O.	$H^{1.74}$ temp. 290°K Field upto 6 K.O. and at 4.2° K $H^{<1.74}$	—	$H^{1.69}$ at 2 K.O. to 7.5 K.O. & $H^{1.88}$ at .35 K.O. to 2 K.O. and all at room temp.
Single Crystal	Current parallel to c-axis and H parallel to Current.	-	—	---	—	$H^{1.62}$ with fields from 1 K.O. to 7.5 K.O. and at room temperatures.

place above a critical field H_c is a consequence of the purity of the crystal, $\Delta R/RH^2$ increasing and H_c decreasing with purity. In view of this we may remark that our specimens were sufficiently pure since we did not observe any H_c even down to 350 Oersteds (Fig. 6). It therefore appears that deviation from H^2 law is a genuine one at least at room temperatures. But before accepting such a view proper consideration of the crystal defects which are naturally present and are further developed in course of chemical purification (crystals used by Soule were also purified in the usual way) should be taken into account.

CONCLUDING REMARKS

The results of the observations reported here have not obviously been discussed in the light of any theory partly because no proper theory for magnetoresistance in anisotropic crystals for transverse and longitudinal cases has yet been developed and partly because observations have not been extended down to low temperatures. Investigations are in progress in these lines and will be published soon.

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